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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01D 53/34 | A1

(11) International Publication Number: WO 91/02582

(43) International Publication Date: 7 March 1991 (07.03.91)

(21) International Application Number: PCT/NL90/00116

(22) International Filing Date: 15 August 1990 (15.08.90)

(30) Priority data:
8902068 15 August 1989 (15.08.89) NL

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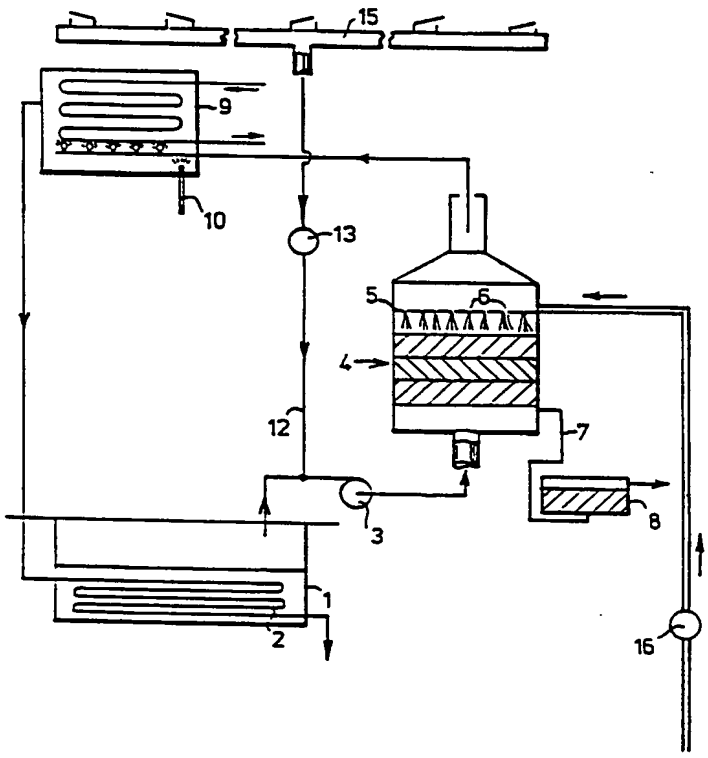
(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LU (European patent), NL, NL (European patent), NO, RO, SE (European patent), SU, US.

Published
With international search report.

(54) Title: PROCESS AND DEVICE FOR PROCESSING MATERIALS FROM WHICH METHANE AND OTHER CHEMICALS, BEING HARMFUL TO THE ENVIRONMENT, MAY ESCAPE

(57) Abstract

Process and device for processing materials from which methane and other chemicals, being harmful to the environment, may escape, e.g. for processing manure or sewage sludge. The starting material is heated and the escaping gases are subjected to a washing treatment with water or a circulating solution of a chemical washed out of the gas, e.g. ammonia. The methane in the gas escaping from the washing device is burned and the developed heat is, at least partly, utilized for heating the starting material.



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Process and device for processing materials from which methane and other chemicals, being harmful to the environment, may escape

In connection with the problem caused by environmental pollution it is of vital importance to remove chemicals, being harmful to the environment, from waste materials.

Considerable amounts of gases, like methane, ammonia and hydrogen sulphide are released during transport, storage and in spreading manure of cows, calve, pigs on the land, and during transport, storage and in processing sludges like sewage sludge. Especially ammonia and hydrogen sulphide are very harmful to the environment.

Ammonia can be oxidized chemically and biologically to nitrous acid and nitric acid, which may cause acid rain.

Hydrogen sulphide is a gas badly smelling after addled eggs and it can be very toxic in high concentration. This substance may also be exposed to oxidation in creating sulphurous acid and sulphuric acid, which are also components of acid rain.

Methane may also cause harm to the ozone layer.

Therefore, it is of vital importance to the environment that these gases, which are harmful to the environment, flow as little as possible freely into the atmosphere at farms.

In broad terms, the invention relates to a process for processing each material, from which methane and other chemicals being harmful to the environment may escape, wherein this material is heated, the escaping gases are subjected to a washing treatment with water or a circulating solution of a chemical washed out of the gas, the methane in the gases escaping from the washing device is burned, and the developed heat is at least partly used for heating the starting material.

A surplus of the heat developed during burning may be used for different heating purposes, e.g. central heating.

The process according to the invention can be used successfully in processing manure and/or feces. When using this process at the farm, one could, if desired, simultaneously withdraw stable air from the stable in which the cattle stay and wash this stable air in counterflow, either or not in the same washing device. In order to obtain a purification, which is as good as possible, water, being as cold as possible is preferred for the washing, for instance water under 12° C. Under these circumstances ammonia and hydrogen sulphide are as much as possible removed from the gases washed in counterflow, since, owing to the low temperature of the water, a large part of the water vapour in the flow of gas, condenses so that this water of condensation dissolves a lot of ammonia also. One can use water from a tank placed in the groundwater as washing water, since this water usually has a low temperature (10° C). Of course, the tank can also be cooled with tap water.

In the washing device, preferably beds of conventional packing units like saddle-shaped units are applied, which improve the contact between the upwards streaming gases and the downwards

flowing water as much as possible. Moreover, it is recommandable to guide the gases in counterflow to the water sprayed thereon, upwards through a condensation tower provided with packing units having decreasing sizes in upward direction.

The ammonia solution collecting at the bottom of the condensation tower, also contains hydrogen sulphide, which is washed out from the gas stream and said hydrogen sulphide may be converted into iron sulphide by passing the solution through iron hydroxide sludge. The iron sulphide formed may be sold to blast-furnaces in order to recover iron from it. If desired, the ammonia may be collected in the water above the layer of sludge as a ammonium hydroxide solution. In using said solution as a circulating washing liquid in the condensation device, the ammonia content of the solution may be increased to even 50%. Subsequently, the solution in the tank may be replaced by clean water.

Of course the process according to the invention can also be applied to manure stored in silos.

As the manure thus treated at the farm does nearly not contain any ammonia and hydrogen sulphide, the manure may subsequently be spread over land in the usual way without, by doing so, a large quantity of chemicals being harmful to the environment flows into the free atmosphere.

In case there is a large surplus of manure the surplus of the manure heated and thickened with the process of the invention can be burned in a combustion over. In that case, the methane gas from which the NH_3 and H_2S are removed can also be burned in the same oven. In that case sulphur oxides and nitrogen oxides, being harmful to the environment, are formed. That is why the gases thus coming from the combustion oven are passed via a heat exchanger through a bed of calcium oxide. The CaO which reacts with the sulphur oxides and nitrogen oxides in the combustion gases is converted into calcium sulphate and calcium nitrate. Moreover, a

mineral residue, containing phosphate is collected at the bottom of the combustion space. This residue provides for a valuable fertilizer, containing calcium, nitrogen and phosphate, when mixing it with calcium sulphate and calcium nitrate formed by binding the sulphur- and nitrogen oxides to CaO.

The invention also relates to plants, which for instance can be sold to farms and which comprise a counterflow washing device with an exhaust at the top for the gases washed which contain methane, said exhaust being connected to a combustion device for burning the methane, which device has an exhaust for the combustion gases being connected to heating tubes which are present in a storage space for the starting material.

The plant may also be situated on board of a ship in which manure of sludge is collected and transported.

In a special embodiment of the device according to the invention the space of a stable is also connected to the gas supply at the bottom of the washing device, because of which the ammonia and the hydrogen sulphide, being present in the exhausted stable air and which would otherwise find their way in the free atmosphere, are recovered therefrom.

If desired, the ammonia solution produced at a farm with the process and device according to the invention, can also be transported to central places, where a concentrated ammonia solution in pure water may be prepared from it, which solution subsequently may be transported to places in need of a concentrated ammonia solution.

The invention also relates to a plant as referred to above, which also comprises a storage silo for the manure and/or feces treated according to the process of the invention, from which silo said material can be supplied to the combustion device by means of a supply device, a heat exchanger connected to the exhaust of the combustion gases of said device, and a container with a bed of

calcium oxide connected to the heat exchanger for the sulphur- and nitrogen oxides from the combustion gases.

The invention is further elucidated in the enclosed figures, which relate to preferred embodiments of the device according to the invention.

In figure 1 heating tubes 2 are provided in the manure storage reservoir 1 (a manure pit or silo). The gases above the manure pit are exhausted by the pump 3 and they are guided at the bottom into the washing device 4. This device contains layers of packing units of decreasing size in upward direction. Above these layers a horizontal pipe 5 provided with openings 6 is situated. The pump 16 supplies water to this pipe, said water having a temperature of e.g. max. 10° C. The washing device 4 is provided with an overflow pipe at the bottom, through which the water solution which is collected at the bottom of the washing device 4 and which contains ammonia and hydrogen sulphide, is passed at the bottom into a bed 8 of iron hydroxide sludge. There, the hydrogen sulphide is converted into iron sulphide. Above this bed the ammonia solution is discharged to a storage.

The gases from which ammonia and hydrogen sulphide are largely removed, but which contain a considerable amount of methane gas are passed into the combustion device 9 in which the methane is burned. When the oven is started or extinguishes, the gas burner 10 can be used to increase the temperature to such a temperature that the methane in the gases, passed through the oven ignites and burns with the oxygen in said gases. The combustion gases are at least partly used to heat the manure in the pit 1, before being discharged into the free atmosphere. For this purpose, they are passed through pipe 20 to the heating tubes 2 of the reservoir 1. If desired, the CO_2 present in said gases can be bound by passing the gas stream through a calcium hydroxide solution.

In the represented embodiment of the device according to the

invention stable air is also exhausted by the pipe 12, which air subsequently is passed into the washing device 4 together with the gases that are exhausted from the manure pit.

This stable air is exhausted from the stable by means of the adjustable fan 13 through a pipe 15, which is arranged in the stable and is provided with adjustable suction valves over its full length.

Figure 2 relates to a version of the above-described device, in which the stable air, exhausted through the pipe 12 and seperated from the gases which are withdrawn from the manure storage reservoir, is passed to a second washing device 4a. In both washing devices 4 and 4a, the gases moving upwards are washed with a circulating ammonia solution, which, from the tank 11 placed in the ground and in which a bed of iron hydroxide sludge is present, is pumped away by the pumps 16. The bed 8 is cooled by ground water or tap water, which is pumped through the pipes 29.

In the oven 9 of both figures 1 and 2, tubes 27 are provided, through which water can be passed, in order to utilize an excess of produced heat for other purposes than the heating of the starting material, for instance for central heating inside the farm. The one way valves 39a and 33a are provided with baffling gauze to prevent the flame from flashing back from the combustion oven. The branch 25A in figure 2 illustrates that a part of the gas washed, and discharged through the pipe 25, can be passed to a gas generator, if desired.

In the pipe 20, a control valve 28 is provided, which is adjusted to the demand of heat in the reservoir 1. The composition of the gas mixture in the combustion chamber 9 can be influenced by means of a control valve 30.

Figure 3 relates to a further development of the apparatus of figures 1 and 2, which enables the burning of a surplus of manure

in the combustion oven 9.

In this plant the surplus of manure is put into the collecting container 21. This manure, treated according to the process of the invention in the manure pit 1 (figures 1 and 2) has a moisture content of about 30 percentage by weight. In the manure pit 1 two layers are formed and after drawing out the methane and other gases by means of heating, the upper layer has a solid content of about 70 percentage by weight. The major part of the phosphate in the manure pit will end in these upper layers. The lower more liquid layer contains much less phosphate and is eventually discharged after it has been dephosphated.

Insofar as the upper layer, which contains much more phosphate, is not immediately used to manure the land, it is conveyed to the container 21. From this container said dry manure is passed into the combustion oven 9 via the conveyor 22. The mineral residue of the manure falls down as ashes through a grate 22 in the bottom of the oven. These ashes consist of phosphate and silicates. Sulphur oxides and nitrogen oxides are also produced by burning the manure in the combustion oven 9. To prevent these oxides from flowing into the free atmoshpere, what would be very harmful to the environment, the hot combustion gases containing the sulphur- and nitrogen oxides are passed through a bed 17 of calcium oxide. This calcium oxide converts the sulphur- and nitrogen oxides into calcium phosphate and calcium nitrate. A heat recuperator 18 and a dust filter 19 are arranged between the combustion oven 9 and the bed 17 of calcium oxide. In the heat exchanger circulating water is heated and the combustion gases from the oven 9 are cooled. In the dust filter 19 beneath the calcium oxide bed, dust is removed from the combustion gas before this gas is passed through the bed 19 of calcium oxide. The calcium oxide of the bed 19 may, if desired, be produced by calcinating lime stone ($CaCO_3$). In that case, e.g. calcite grains ($CaCO_3$ containing only 0.5% water) originating from water softening plants can be brought into the oven 9 together with the manure to be burned. These grains are

calcinated at the high temperature prevailing in said oven. The CaO formed is collected together with the mineral components of the manure in the bottom of the oven. The mixture of CaO, phosphate and silicates can be used in the bed 19 for binding the sulphur- and nitrogen oxides in the combustion gases. This results in a conversion of CaO into calcium phosphate and calcium nitrate. The mixture of phosphate, sulphate and nitrate and calcium product may be utilized as fertilizer.

In the plant according to figure 3 the water heated in the heat exchanger is passed through the pipe line 20 into the heating tubes in the silo 1 (see figures 1 and 2) to heat the manure therein, and, may, in addition, e.g. be used in a central heating device 30 or for the heating of a boiler 31.

In case the CH_4-gas coming from the washing tower is also utilized for a combustion engine 24 of a gas generator, one does not mix this CH_4-gas, supplied through pipe line 25, in advance with the gas mixture of $CH_4 + O_2 + N_2$, withdrawn from the stable and washed in the washing tower and which gas is supplied via pipe line 26 in order to prevent the nitrogen oxides in the latter gas stream from attacking the metal of the turbine of the gas generator.

C L A I M S

1. Process for processing a material from which methane and other chemicals, being harmful to the environment, may escape, **characterized in that** the material is heated and the escaping gases are subjected to a washing treatment with water or a circulating solution of a chemical washed out of the gas, and the methane in the gases escaping from the washing device, is burned and the developed heat is, at least partly, utilized for heating the starting material.

2. Process according to claim 1, **characterized in that** the starting material contains ammonia and the washing is effected with a circulating ammonia solution.

3. Process according to claim 2, **characterized in that** manure and/or feces are (is) used as starting material(s).

4. Process according to claim 3, **characterized in that** stable air, withdrawn from a stable in which cattle stay, is subjected to a washing treatment with water or a circulating ammonia solution, simultaneously with the gases extracted from the space in which manure and/or feces are (is) heated.

5. Process according to claim 2, **characterized in that** the starting material is sewage sludge.

6. Process according to any of the preceding claims, **characterized in that** one washes with a washing liquid having a temperature not exceeding 12 °C.

7. Process according to any of preceding claims 2-6, **characterized in that** hydrogen sulphide being present in the ammonia solution obtained during washing is removed from said solution by passing the solution through an iron hydroxide sludge.

8. Process according to any of the preceding claims, **characterized in that** starting material which is heated according to the process of claim 1, is also burned in the combustion oven in which methane is burned, after which the combustion gases are cooled by heat exchange, and passed through a bed of calcium oxide to bind the sulphur- and nitrogen oxides before releasing them into the free atmosphere.

9. Process according to claim 8, **characterized in that** the calcium sulphate and calcium nitrate, formed by the reaction of the calcium oxide with sulphur- and nitrogen oxides in the combustion gases, are mixed with the phosphate-containing residue discharged from the bottom of the oven, in order to obtain a fertilizer, containing calcium, phosphate and nitrogen.

10. A plant to carry out the process according to any of the preceding claims, comprising a counterflow washing device having an exhaust at the top for the washed gases, containing methane, said exhaust being connected to a combustion device for burning the methane, which device has an exhaust for the combustion gases being connected to heating tubes, which are present in a storage space for the starting material.

11. A plant according to claim 10, in which a stable is also connected to the gas supply at the bottom of the washing device or to a seperate washing device, from which the escaping gases are also supplied to the combustion device.

12. A plant according to claim 10 or 11 **characterized by** a storage silo for the manure and/or feces treated according to the process of claim 1, from which said material can be brought into the combustion device by means of a supply device, a heat exchanger connected to the exhaust for the combustion gases from said device, and a container with a bed of calcium oxide connected to the heat exchanger for removing the sulphur oxides and nitrogen oxides from the combustion gases.

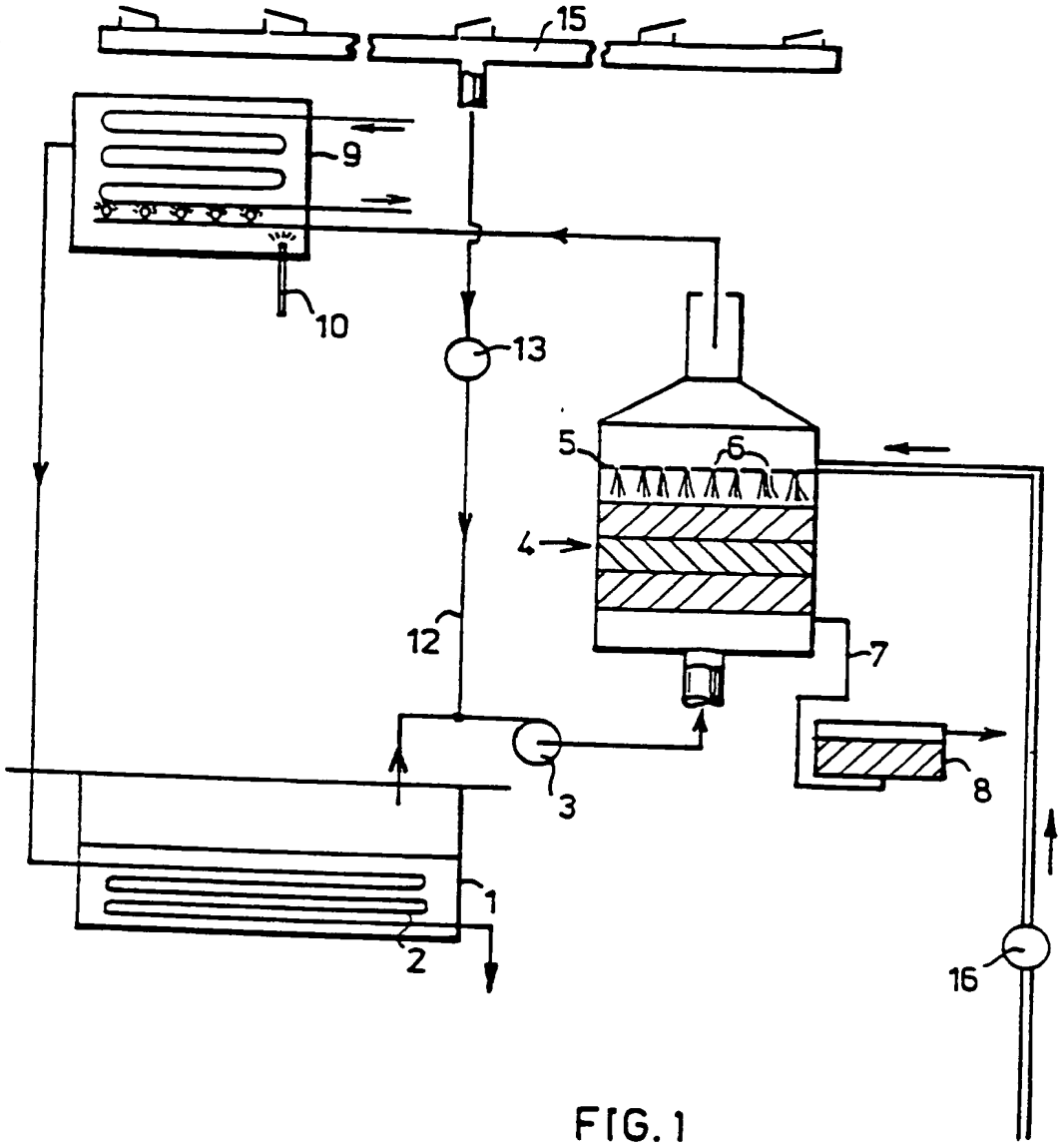

FIG. 1

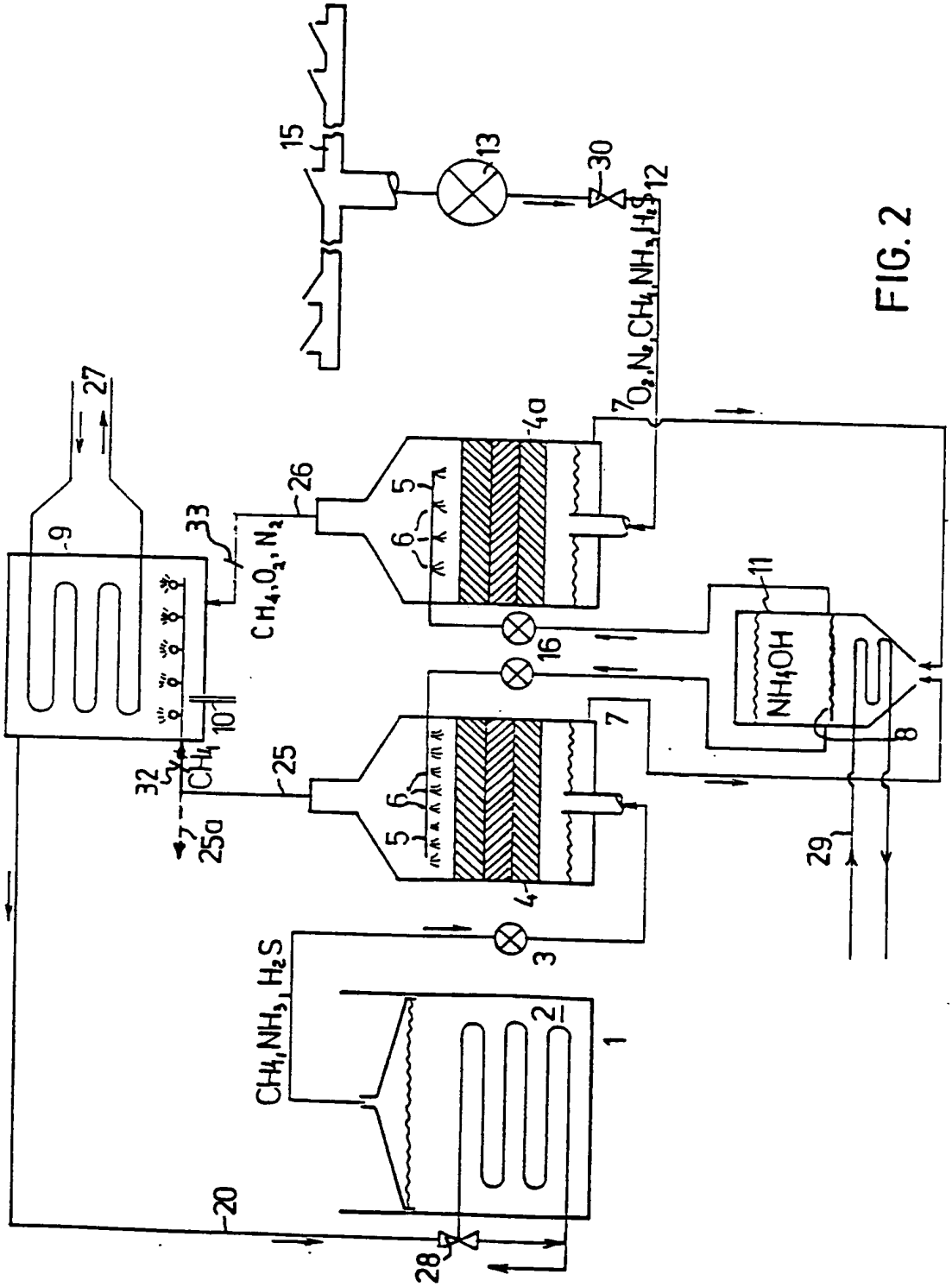
15
13
30
12
$O_2, N_2, CH_4, NH_3, H_2S$
27
9
33
26
5
6
4a
CH_4, O_2, N_2
11
16
NH_4OH
10
32
CH_4
25
7
8
25a
5
6
4
29
3
CH_4, NH_3, H_2S
2
1
20
28

FIG. 2

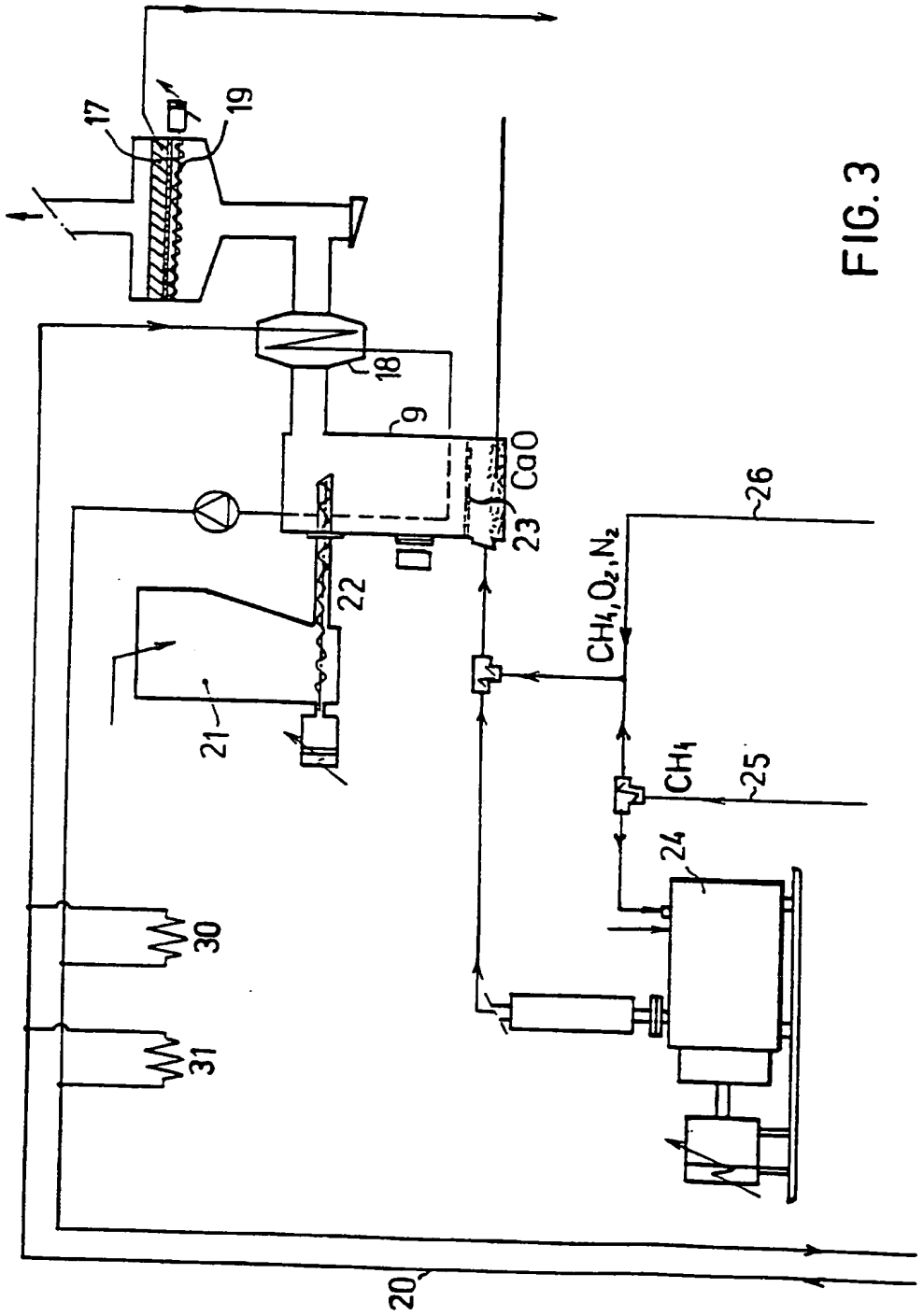

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 90/00116

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: B 01 D 53/34

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	B 01 D, C 02 F, C 05 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	Patent Abstracts of Japan, volume 5, no. 205 (C-85)(166) 24 December 1981, JP, A, 56126490 (HIGUMA KOUKI K.K.) 3 October 1981 see the abstract	1,3,4
A	DE, A, 3709521 (VEB KOMBINAT ILKA LUFT- UND KÄLTETECHNIK) 12 November 1987	
A	NL, A, 8602150 (GRONTMIJ) 16 March 1988	

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
5th November 1990	20. 11. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	miss T. MORTENSEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. NL 9000116 SA 39291

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/11/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 3709521	12-11-87	None	
NL-A- 8602150	16-03-88	None	